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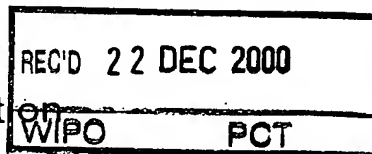
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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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PEROXIDE-TREATED PRODUCTS WITH NO BLOOMING

5 The present invention relates to compositions comprising peroxide and a specific copolymer, a process involving the use of peroxides and said copolymer to treat elastomer/polyolefin compositions, and the products obtained by this process. The resulting treated products show essentially no blooming and reduced emission of volatile compounds. Preferably, said
10 treatment involves the degradation and/or cross-linking of predominantly a polyolefin or elastomer through reactions initiated by radicals obtained by decomposition of the peroxide. The resulting treated products can be in the form of finished articles or intermediates.

15 Typically, products that are obtained through, *inter alia*, a peroxide-initiated treatment, such as a cross-linking process or a degradation process, suffers from blooming of the decomposition products of said peroxide. Furthermore, said decomposition products can be quite volatile in nature and hence be emitted from the treated article/intermediate. Since such blooming/emission is
20 undesired, several solutions have been put forward to reduce these phenomena. US patent No. 3,420,891, for instance, proposes to prevent blooming by using certain tris-peroxides. Belgium patent No. 883.693, on the other hand, proposes to use phthalic anhydride in an elastomer composition. According to a non-binding theory as described in this patent, the phthalic
25 anhydride reacts with an OH group-bearing decomposition product of the peroxide. While the OH group-bearing decomposition product would lead to blooming, the reaction product with the phthalic anhydride does not. The phthalic anhydride was used in a quantity of at least 2 moles per mole of (difunctional) peroxide used.

30

The use of phthalic anhydride, however, has its drawbacks. More particularly,

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It cross-linking or degradation, so that recipes do not have to be changed other than in adding a certain ingredient.

5 There has been an ongoing search for peroxide-containing compositions that will satisfy those needs. Surprisingly, we have found that the combination of peroxides and specific olefinic copolymers according to the invention is particularly suitable, and that the use of such a combination leads to a cost-efficient treatment process without significant recipe changes being necessary. The resulting products show essentially no blooming, and the emission of
10 volatile products from the product was reduced in comparison with products wherein the peroxide was used without said polymer/elastomer being present.

The invention is characterized in that peroxide is used in combination with one or more copolymers comprising olefin-derived moieties and one or more
15 anhydride and/or acid groups, the copolymer being used in a quantity of from 0.1 to 500 per cent by weight of the weight of the peroxide.

It is noted that Japanese patent application No. 08157646 discloses the use of such copolymers in elastomer compositions that contain brass and/or brass-plated iron in order to improve the adhesion of the elastomer, after peroxide-initiated vulcanization, to said brass. Such compositions are not the subject of
20 the present invention. Furthermore, this Japanese patent application is silent with respect to blooming/emission of volatile products.

25 The copolymers containing olefin-derived moieties and anhydride and/or acid groups can be suitably obtained through (random) copolymerization or grafting processes. EP-A-0 429 123, for instance, discloses a suitable process wherein olefins (1), or mixtures of olefins, are reacted with α,β -unsaturated dicarboxylic compounds (2), in the presence of a polymerization inhibitor, and preferably in

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acid; itaconic acid; citraconic acid; and other anhydrides and/or acids with an unsaturated group that can be linked with an olefin.

5 Preferably, the copolymer contains anhydride and/or acid groups derivable from maleic anhydride or methacrylic acid. The copolymers might also be adducts of alkadiene polymers and cyclic or acyclic anhydrides of mono- or dicarboxylic acids containing 4 to 18 carbon atoms as disclosed in US patent No. 4,423,177.

10 Although it is not critical, the copolymers preferably have a composition as obtainable by reacting one or more olefins and one or more anhydride/acid group-containing monomers, with the anhydride/acid group-containing monomers being present in a quantity of 5-75 per cent by weight (%w/w). More preferably, the anhydride/acid group-containing monomers are present in a quantity of 10-50 %w/w.

15 The copolymers were found not to bloom from products comprising them, possibly due to their molecular weight. To avoid blooming, the molecular weight of the copolymer must be over 500, preferably over 800, and more preferably over 1100 Dalton. However, in order to facilitate processing of compositions comprising the copolymer, and to allow for sufficient mobility of the copolymer in the final matrix, the molecular weight of the copolymer must be below 50,000, preferably below 25,000, and more preferably below 15,000. Typically, an alternating copolymer with 5 to 50 repeating units can suitably be used.

25 The quantity of said copolymer that is to be used in the peroxide-containing elastomer/polyolefin compositions can vary over a wide range and can be optimized on the particular composition and the conditions during peroxide decomposition. However, since the copolymer does not bloom at all, it can be used in a more than stoichiometric quantity, based on the quantity of OH group-

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is meant to denominate all thermoplastic and/or rubbery polymers. Preferably, the polymer/elastomer is a (co)polymer of propylene and/or a synthetic or natural rubber, including polypropylene (PP), ethylene/propylene copolymers (such as EPM and EPDM), ethylene octene copolymers (EOP), polybutadiene rubber (BR), styrene butadiene rubber (SBR), nitrile butadiene rubber (NBR), hydrogenated nitrile butadiene rubber (HNBR), polychloroprene rubber (CR), silicone rubber (VMQ, MQ), fluoro elastomers (FKM), natural rubber (NR), and thermoplastic vulcanizates (TPV). Preferred types of polymer/elastomer include EPM; EPDM, such as Vistalon®606 and Vistalon®7500 ex Exxon and

10 Buna®EP 6550 and Buna®EP G8450 ex Bayer; EOP, such as Engage®8150 and Engage®8180 ex DuPont-Dow-Elastomer; VMQ, such as Silopren®HV ex Bayer; FKM, such as Viton® products ex DuPont Dow Elastomers, and particularly PP, such as Hostalen®PPT 1070 ex Hoechst. Most preferred are compositions based on synthetic rubbers, since here the blooming

15 phenomenon is most pronounced, such as EPM, EPDM, and EOP.

It is furthermore to be understood that the term "blooming" is used as it is conventionally in the art. Blooming typically is the result of products migrating to the surface of a polymeric/elastomeric article. Whether a product is subject to

20 blooming or not depends on the solubility of the compound and the rate of diffusion. As is conventional, products are considered not to bloom when no changes on the surface are observed (visual inspection) upon storage for a prolonged time at temperatures above the temperatures that may be encountered during projected use of the products.

25

The peroxide as used in the compositions according to the invention can be any conventional peroxide. Preferably, the peroxides are chosen from products conventionally used in cross-linking and degradation reactions, such as dialkyl peroxides, perketals, peroxyarbonates, peroxydicarbonates, and thiol. More

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mentioned below, and copolymer with olefin-derived moieties and anhydride and/or acid groups. Typically, such compositions will contain 1-99.9% by weight, based on the total weight of the composition, of additives and/or carrier material and 99-0.1% by weight, based on the weight of the composition, of the copolymer, up to a total of 100%. More preferably, the compositions will contain 10-99% of additives and/or carrier material and 90-1% of the copolymer. Preferred compositions comprise copolymer with olefin-derived moieties and anhydride and/or acid groups, one or more fillers selected from the group consisting of silica, clay, chalk, kaolin, and carbon black, and optional further conventional additives mentioned above.

The treatment of the present invention most often will involve a radically induced cross-linking and/or degradation process. However, depending on the presence of further additives, such as co-agents, monomers, chain transfer agents, initiators, such as NO compounds, also grafting, functionalization and/or chain transfer reactions can be the (main) reason for said treatment. The compositions according to the invention are preferably used in grafting, degradation and/or cross-linking reactions.

The products obtainable by this process, which show essentially no blooming and reduced emission of volatiles, are typically but not limited to: building profiles; automotive profiles; such as sponge door seals and weatherstrips; mechanical goods, such as hose, conveyor belt cover materials, and seals; and the like. Again, the products may be in the final form and shape, or be present as an intermediate that needs further processing. Such an intermediate may be a granulate of treated polymer/elastomer.

As stated above, compositions according to the invention can contain further compounds, such as the usual additives and fillers. Examples of such additives

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MW = molecular weight (of anhydride)

Px-14R = Perkadox® 14 R, 50% by weight of peroxide.

Px-14 = Perkadox® 14 40 B pd, 40% by weight of peroxide

PX-200 = Dapral® PX 200

5

Procedures:

Unless stated otherwise, a standard 100 / 50 / 10 compound (100 parts by weight rubber, 50 parts by weight carbon black, and 10 parts by weight paraffin oil) was used as the polymer/elastomer for testing purposes. Compounding, in a 5-litre internal mixer ex Werner & Pfleiderer, of 1.6 kg Keltan® 520, 0.8 kg carbon black SRF N-772, and 0.16 kg Sunpar® 150, produced this standard compound.

15

Further ingredients, i.e. peroxide and reactive additive, were used in said standard compound for evaluation. The ingredients were incorporated into the compound on a two-roll mill (Schwabenthal 150x350mm) at a starting temperature of about 50°C. The cross-linking of the resulting 2 mm rubber sheet was done by compression moulding at 175°C for 15 minutes, in which step virtually all peroxide was decomposed.

20

The extractable matter in the rubber, after cross-linking, was determined by extraction with dichloromethane and subsequent GC-analysis. The quantity of extractable matter is an indication of the likelihood that the treated product will show blooming or emit volatile matter.

25

Some products were evaluated using dynamic head space GC analysis to determine the quantity of volatile matter in the product. To this end, a sample of 30-50 mg of the product was heated in a glass tube under a stream of inert gas. The desorbed volatile compounds were trapped in a liquid nitrogen cooled trap

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Table 1

Example	Additive (Copolymer)	MW (Dalton)	Added (g)	MAH (meq)	Blooming of peroxide / additive	
					1 week	1 month
A	None	-	-	-	Yes	Yes
B	succinic anhydride	100	2	20	Yes	Yes
C	phthalic anhydride	148.1	2	13.5	Yes	Yes
D	1,2 4,5 benzene-tetra carbacid	254	2	15.7	Yes	Yes
E	cis-hexahydro phthalic anhydride	154	1.2	7.8	No	Y s
F	Methylnorbornene-2,3 dicarboxylic anhydride	178	1.4	7.8	No	Y s
1	PX-200 1/1	(308) _n	3	9.75	No	No

From the product of Example 1, in total about 1,000 ppm of $\text{CH}_3\text{C}(\text{O})\text{-C}_6\text{H}_4\text{-C}(\text{CH}_3)_2\text{-OH}$ and $\text{HO-C}(\text{CH}_3)_2\text{-C}_6\text{H}_4\text{-C}(\text{CH}_3)_2\text{-OH}$ could be extracted, whereas
 5 Comparative Examples A, E, and F showed extractable levels of these compounds of 3,500-5,500 ppm. Comparative Examples B-D showed low levels of extractables, due to the high amount of anhydride/acid used. However, in these tests the excess anhydride/acid bloomed from the product.

Head space GC analysis using cycles A and B showed the product of Example
 10 1 to contain about 500 and 1,700 ppm toluene, respectively, while the product of Comparative Example A contained 1,100 and 3,500 ppm toluene, respectively. Each number is the average result of two samples.

Examples 2-5 and Comparative Examples G and H

15 The previous examples were repeated, except that 4.2 g of Px-14 (4.96 mmol) were used per 160 g of standard compound. The total quantity of extractable

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peroxyisopropyl)benzene (5 mmol) were used per 160 g of standard compound. In Comparative Example I no copolymer was used, while Example 6 used 2 g of PX-200 1/1. After one month the product of Comparative Example I showed blooming, while the product of Example 6 did not.

- 5 When analyzed for extractable/volatile matter, the product of Example 6 showed that a total of 2,180 ppm of $C_6H_5-(C(CH_3)_2-OH)_3$ and $CH_3C(O)-C_6H_5-(C(CH_3)_2-OH)_2$ could be extracted, while the product of Comparative Example I contained 4,500 ppm of such extractable compounds.

- Head space GC analysis using cycles A and B showed the product of Example 10 6 to contain 150 and 850 ppm toluene, respectively, while the product of Comparative Example I contained 165 and 1,700 ppm toluene, respectively. Each number is the average result of two samples.

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norbornene-2,3-dicarboxylicanhydride, (meth)acrylic acid, maleic acid, fumaric acid, itaconic acid and/or citraconic acid, preferably from maleic anhydride or methacrylic acid.

5 6. Products obtainable by the process of any one of the preceding claims.

7. Compositions comprising:

- 5-70% by weight, based on the total weight of the composition, of one or more peroxides,
- 10 - 0.1-500% by weight, based on the weight of the peroxide(s), of a copolymer with olefin-derived moieties and anhydride and/or acid groups,
- optional further additives, and
- 0-50% by weight of a carrier material,

15 which are suitable for use in the process of claim 1.

8. Composition according to claim 7 wherein the copolymer has a molecular weight from 500 to 50,000.

20 9. Composition according to claim 7 or 8 wherein the copolymer comprises olefinic units derived from propylene, butadiene, isobutylene and/or C₆ to C₂₄ α-olefins, preferably C₁₂ to C₁₈ olefins, and anhydride/acid groups derived from maleic anhydride; (di)alkyl/aryl-maleic anhydride; such as n-dodecylmaleic anhydride, citraconic anhydride, and maleic phenyl
25 anhydride; (substituted) norbornene-2,3-dicarboxylicanhydride; (meth)acrylic acid; maleic acid; fumaric acid; itaconic acid and/or citraconic acid, preferably from maleic anhydride or methacrylic acid.

10. Composition according to any one of claims 7-9 wherein the copolymer

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Abstract

The invention relates to the use of copolymers comprising olefin-derived as well as anhydride and/or acid moieties in the treatment of polymers/elastomers using free radicals obtained by decomposing a peroxide. Products resulting from such a treatment show essentially no blooming and reduced levels of volatile compounds, compared to products obtained from the same treatment in the absence of said copolymer.